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(54) IMPROVEMENTS IN OR RELATING TO CLEANING COMPOSITIONS

VERBESSERUNG IN ODER IN BEZUG AUF REINIGUNGSMITTEL

AMELIORATIONS CONCERNANT DES COMPOSITIONS DE NETTOYAGE

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Description

Field of the invention

This invention relates to cleaning compositions and concerns compositions including a component for disclosing the presence of otherwise invisible soil generally mainly of organic origin, and a component for cleaning soil. The invention also concerns a method of cleaning.

Background to the invention

Soil (ie dirt or contamination) of mainly organic origin typically comprises protein, carbohydrate and/or fat, and is generally associated with bacterial or microbial contamination which may present a risk to health. In order to visualise soil it is convenient to use a reagent, such as certain dyes, which binds protein. By disclosing protein-containing soil, the location of associated bacterial or microbial contamination can be indirectly visualised and can be targeted for effective cleaning.

JP 63/159758 (Oguri) concerns toilet seat cleaning compositions and has as its stated objective provision of a composition which will clean and reveal soil on toilet seats. However, the document does not teach how to achieve this objective.

The Oguri compositions are stated to contain a component which is coloured on reaction with protein or lipids, so that the appearance of the colour is intended to indicate the presence of protein or lipid. Ninhydrin is given as an example of reagent that becomes coloured on reaction with protein. As stated in the document, ninhydrin turns reddish violet on reaction with amino acids. Ninhydrin does not react with proteins, but instead reacts with amino acids. As ninhydrin does not bind to or react with protein, the reagent is not an effective indicator of the presence of protein.

In the Oguri Examples, experiments were performed using a glass plate onto which the palm of a hand had been pressed. Ninhydrin reacts with amino acids and ammonia components present in sweat from palm, and not protein, so that the development of the colour is indicative not of the presence of protein soil, but of palm sweat.

The Oguri composition may include optional dyes such as Rose Bengal for an unspecified purpose, presumably to make the products look attractive.

The Oguri compositions are described in general terms as including a surfactant for cleaning purposes, eg polyoxyethylene (30) cetyl ether, and optional solvent, eg ethyl alcohol.

The detailed examples concern experiments with a range of different formulations, as specified in Tables 1 and 2. None of these formulations includes a dye such as Rose Bengal. Further, even assuming that ninhydrin is treated as the protein disclosing agent (which in fact it is not) there is no example of a formulation comprising ninhydrin, surfactant and solvent. Examples 1 to 19 include either surfactant or alcohol but not both. The Examples of Table 2 do not include ninhydrin.

There is thus no enabling disclosure in Oguri of three component formulations comprising dye which binds to protein, solvent and surfactant.

WO90/14591 (Cleansolve International APS) discloses the use of a range of dyes, particularly acid dyes such as Erythrosin BS (E127), for disclosing soil, in combination with a cleaning agent of unspecified nature.

However, this specification does not discuss the problems that arise in practice when combining a dye with a cleaning agent for use in disclosing soil. In particular, the present inventors have found that while solutions of certain dyes in water alone will bind to protein, and so are effective in disclosing soil, mixtures of the dyes with a range of surfactants typical of those used in general purpose hard surface cleaning formulations at typical (user) concentrations are unable to reveal the presence of protein. Thus it appears that the presence of surfactant can prevent the dyes from binding to, and revealing, protein. It is known that surfactants bind protein, with anionic surfactants binding more strongly than non-ionic surfactants. One possible explanation of the observed behaviour is that the surfactant competes with the dye molecules for binding sites on the protein. Another possible explanation is that solubilisation of the dye in surfactant micelles simply reduces their affinity for the protein.

US 5039441 (Thomas) discloses acidic, aqueous hard surface cleaners having a pH in the range 1 to 4 for removing greasy soil, limescale and soap scum, particularly from non-acid resistant surfaces, eg. zirconium white enamel (also known as European enamel). The cleaner is preferably in the form of a spray-on microemulsion, and comprises a mixture of anionic and non-ionic (eg. alcohol ethoxy sulphates) organic detergents and various other essential ingredients including carboxylic diacids, phosphoric acid and amino alkylene phosphonic acid. Optional ingredients are listed in column 5, and include co solvents, dyes and adjuvants including perfumes. Column 7 lines 47 to 50 states that perfume is normally present in an amount in the range 0.2 to 2%, of which at least 0.1% is terpene or terpineol. The terpineol is alpha-terpineol and is preferably added to allow a reduction in the amount of perfume.

There is no discussion of the optional dye. Although Example 3 happens to use the protein-substantive dye CI Acid Blue 104, this is purely incidental. The dye is there as a colourant only and there is no teaching of the dye binding

to soil.

Further, the specific formulations described in the Examples of Thomas would not function to reveal protein, even if they did use protein-substantive dyes, because of the presence of excess anionic surfactant. In Example 1 the surfactant includes more than 50% of anionic surfactant (1% of sodium paraffin sulphonate and 3% of sodium lauryl ether sulphate (both of which are anionic), with 3% of alcohol ethoxylate detergent (which is non-ionic)). With such a composition the anionic surfactant will bind strongly to protein, competing with the dye. The dye (even if protein substantive) will thus be prevented from binding to protein and revealing soil. The only possible solvent present in Example 1 is 1% of perfume.

Example 2 is generally similar to Example 1.

Examples 1 and 2 just refer generally to blue dye without reference to a dye that is protein-substantive.

Example 3 specifically includes 0.001% (10ppm) of the protein-substantive dye CI Acid Blue 104, although the protein-substantive properties of the dye are completely incidental. The Example 3 formulation also includes 6.67% of anionic surfactant (paraffin sodium sulphonate - Hostapur SAS) and 3% of non-ionic detergent (Plurafac RA-30). The anionic surfactant will act to prevent the dye from binding to protein, as discussed above. The only possible solvent is provided by the perfume and perfume substitute. The perfume substitute used is alpha-terpineol which is a solid at room temperature.

Thus none of the Examples in Thomas concerns a formulation which would function to reveal soil, as in the present invention. Further, it is not clear how these formulations would be modified so that they would reveal soil, and indeed there is no motivation so to do.

Surprisingly, the present inventors have found that dye can bind to, and reveal, protein when the dye is present in suitable mixtures of dye, surfactant and solvent.

Summary of the invention

Thus, in one aspect the present invention provides an acidic aqueous hard surface cleaning composition comprising dye which is substantive to protein; water-miscible solvent; and surfactant, the composition being effective to clean a surface and also to indicate the present of soil remaining on the surface by binding of dye to protein.

It is found with such compositions, the dye can bind to protein to form a visible coloured complex and so reveal soil, with the surfactant (and also to some extent the solvent) performing a cleaning function to remove soil. By visualising protein, soil can be targeted for cleaning. Any dye remaining visible after cleaning indicates imperfect cleaning.

Statistical analysis of experimental results indicates that the presence of increasing amounts of solvent or surfactant alone in a mixture with dye reduces the binding of dye to protein, yet with three component mixtures of dye, surfactant and solvent, although the extent of binding of dye to protein is reduced as compared with that of dye in water alone, the reduction in binding of dye is less than would be expected from the combined effects of surfactant and solvent. The surfactant and solvent together thus have a synergistic effect the result of which is to lower the reduction in binding of dye to protein.

Dye is thus capable of binding to and revealing soil from suitable mixtures of dye, surfactant and solvent, and such mixtures are also capable of effective cleaning of soil. The invention can thus provide a composite formulation capable of revealing and cleaning soil.

Good results have been obtained with acid dyes in acidic compositions. Acid dyes are a well known class of dye which are widely used for various purposes including dyeing of wool, colouring of food etc.

Acid dyes of the triphenylmethane type that are substantive to, ie capable of binding to, protein (and wool), include Brilliant Blue G (also known as Acid Blue 90, C.I. 42655), Brilliant Blue R (Acid Blue 83, C.I 42660), C.I. Acid Blue 104, C.I. Acid Blue 109 and Acid Violet 17 (C.I 42650). Of these dyes, Brilliant Blue G is currently preferred.

Acid dyes of the xanthene type that are substantive to protein include Erythrosin B (Acid Red 51, C.I. 45430) and Rose Bengal (Acid Red 94, C.I. 45440). These dyes have been used as food colourants (Erythrosin B is Food Red Colour No 14 and Rose Bengal is Food Red Colour No 105) and so are well suited to use in compositions intended for household use. Erythrosin B is also on the list of colouring agents permitted for use in all cosmetic products (see EEC Directive 76/768/June 1991 annex IV - Part 1, page 4, No E127).

Further acid dyes that are substantive to protein include phthalocyanine sulphonates, such as aluminium phthalocyanine sulphonate (APS) (eg available from Ciba Ltd under the trade mark Tinolux BBS), and zinc phthalocyanine sulphonate (ZPS).

For dye structures and other details, see The Sigma-Aldridge Handbook of Stains, Dyes and Indicators, F J Green, Aldridge Chemical Co., Inc (1990).

It is preferred to use a dye the colour of which is fugitive, ie the colour of which disappears (and so becomes at least substantially invisible to the naked eye) under suitable conditions. The coloured dye/protein complex preferably also behaves in a similar manner, at least substantially losing its colour under similar conditions, so that any remaining bound dye also becomes colourless. The conditions can be either naturally occuring or controlled by the user, and

include the following: chemical reaction with acid or base; oxidation (eg by atmospheric oxidation or bleach); photochemical reactions; physical displacement reactions.

The acid dyes mentioned above are all photosensitive to a greater or lesser extent, especially at the concentrations required for disclosure. Rose Bengal and Erythrosin B are especially preferred as these dyes fade relatively quickly. Mixtures of the (red) xanthene dyes and (blue) triphenylmethane dyes may be used in which fading of the blue dye may be accelerated by concomitant Type II sensitised photo-oxidation (see Kirk-Othmer, Encylopaedia of Chemical Technology, (Third Edition), Vol, 8, page 405, Wiley-Interscience publication, John Wiley & Sons (1979) for a summary of dye-sensitized reactions) and for which light absorption in the visible spectrum is maximised for a given amount of dye.

Brilliant Blue G is also very sensitive to oxidation with consequent colour loss on exposure to chlorine bleach such as sodium hypochlorite, eg as present in commercially available bleach preparations such as Domestos bleach and bleach-containing preparations such as Domestor Multi-Surface Cleaner (Domestos is a Trade Mark).

Use of a fugitive dye has the advantage of any unbound dye remaining after use will become at least substantially colourless under appropriate conditions. In addition, any dye absorbed into porous material during use, such as in grouting or in scratches in work surfaces, can be prevented from forming a permanent or long term undesirable stain.

It is also preferred to use a dye which is capable of photo-dynamic inactivation of micro-organisms. Preferred dyes are those which generate singlet oxygen on exposure to light. Excitation of the dyestuff by visible light to a first excited state is followed by inter-system crossing to the triplet state. On subsequent collision with molecular oxygen, electronic energy transfer occurs, returning the dyestuff to the ground state and generating singlet oxygen.

Photo-oxidation of any vital component of an organism may result in cell death (protein, polypeptide, amino-acids, lipids with allylic hydrogens, tocopherols, sugars and cellulose).

Certain of the acid dyes mentioned above, particularly Rose Bengal, Erythrosin B, APS and ZPS, satisfy these requirements and generate singlet oxygen on exposure to light. These dyes are also substantive to protein, as noted above, and so are capable of binding to micro-organisms, typically by binding to cellular protein on the organism surface. This has the advantageous consequence that the dye can bind close to the target micro-organisms thus enhancing the effectiveness of singlet oxygen (which has a short lifetime and therefore a short pathlength for diffusion) against the target organisms. This thus enables targetted killing of micro-organisms with a consequent germicidal and disinfecting effect.

The composition is preferably acidic, typically having a pH in the range of 3 to 5, eg a pH of about 4, as acidic compositions are found to have substantially enhanced effectiveness against Gram-negative micro-organisms as compared with neutral compositions. The effectiveness against Gram-positive micro-organisms seems not to be significantly affected by pH. The composition is conveniently made acidic by use of relatively mild organic acid, such as acetic acid.

A synergistic effect, similar to the synergistic effect discussed above concerning binding of dye, is also found to apply to the phototoxic effect of dyes in admixture with solvent and surfactant.

Further, certain solvents, eg ethanol, weaken the cell walls of micro-organisms, making them more permeable and so more susceptible to penetration by singlet oxygen. This has the effect of enhancing the micro-organism-killing effect of the dye.

The photo-dynamic inactivation of micro-organisms in suspension by dyes such as Rose Bengal is known. However, it is surprisingly found that suitable dyes are capable of photo-dynamic inactivation of micro-organisms on surfaces. It is well-known that micro-organisms are much more susceptible to biocides in their planktonic or suspended state: they are much more difficult to inactivate when attached to surfaces, which is their usual or preferred state. Micro-organisms will normally be on surfaces in the form of "biofilms", that is, embedded in a matrix of extracellular material. This extracellular material may sometimes be referred to as "adhesin" in the literature. It is therefore not obvious that a process which acts on micro-organisms in their planktonic state would act on surface-bound organisms without modification being required. Surface-bound micro-organisms represent an important and substantial source of contamination in domestic, institutional and industrial environments, and the present invention can enable targetted germicidal action on such micro-organisms.

Mixtures of dyes can be used in compositions in accordance with the invention if appropriate, for example to produce dyes having improved light absorption properties (eg to maximise the light absorbed for a given (total) amount of dye), desired fugitive properties, desired colours etc.

The composition typically includes dye in an amount in the range 10 to 100 ppm, eg 20 ppm.

The solvent is preferably polar and is preferably a straight or branched chain C2 to C5 alcohol such as ethanol, butanol, isopropanol (propane-2-ol) (IPA), N-butoxy propan-2-ol (propylene glycol n-butyl ether), 2-butoxy ethanol (ethylene glycol monobutyl ether). IPA is one currently preferred solvent.

Dihydric alcohol such as ethylene glycol, and water miscible ethers such as dimethoxyethane, eg 1, 2-dimethoxyethane, may also be used.

Mixtures of solvents can be used if appropriate, eg mixtures of ethanol and N-butoxy propan-2-ol.

Solvent is preferably present in an amount in the range 2 to 20% by weight of the total weight of the composition.

The surfactant is preferably alkoxylated, more preferably ethoxylated, eg being in the form of ethoxylated alcohols. The alcohol preferably has between 4 and 15 carbon atoms, is of straight or branched chain configuration, and has an BLB value (hydrophilic lipophilic balance) in the range 10 to 14, eg 12.

A wide range of suitable surfactants are commercially available, one such material being the surfactant available under the trade name Imbentin 91-35, from Kolb, which is a non ionic C9-11 alcohol ethoxylate, having an average of 5 moles of ethylene oxide per mole of alcohol.

Primary ethoxy sulphates may also be used.

Mixtures of surfactants may be used if desired.

The surfactant is preferably non-ionic or predominantly non-ionic although a small amount of anionic surfactant can optionally be included. The inclusion of anionic surfactant will have the effect of improving the cleaning power of the composition while reducing the disclosing power.

Preferred anionic surfactants for this purpose include primary alkyl sulphates (PAS), preferably sodium dodecyl sulphate (SDS). Commercial mixtures containing a substantial proportion of dodecyl sulphate (eg Empicol LX Empicol is a Trade Mark) are especially preferred. Dodecyl sulphate is a known protein denaturant, is good for cleaning protein off surfaces, and is biocidal.

The weight ratio of non-ionic to anionic surfactant is preferably at least 3:1.

The composition is preferably substantially free of cationic surfactant, but may include a minor amount of cationic germicide.

Surfactant preferably constitutes an amount in the range 0.05 to 2.5% by weight of the total weight of the composition, typically 0.5% to 1.5% by weight, eg 0.7% by weight non-ionic surfactant with an optional amount of up to 0.2% by weight of anionic surfactant.

The composition may include a number of optional ingredients including the following:

1. Detergent boosters, preferably metal chelating agents such as ethylene diamine tetra acetic acid (EDTA). Metal chelating agents (including EDTA) have also been claimed to permeabilise cell walls, thus making organisms more susceptible to the biocidal effect of singlet oxygen

2. Electrolyte such as a buffer or salt, eg Na_2SO_4, which acts to assist binding of dye to protein by promoting movement of dye from the aqueous phase to the protein salt. Electrolyte is commonly present in acid dye formulations as commercially available, although additional electrolyte can be added if required. Total electrolyte content of the composition would typically be in the range 0 to 1% by weight, preferably about 0.1%.

3. Perfumes.

4. Thickners.

The composition is in the form of an isotropic, single phase composition and is of particular use in hard surface (eg glass, plastics, ceramic and metal surfaces) cleaning, finding application in a wide range of contexts, including domestic cleaning, eg of kitchen and bathroom surfaces including toilet bowls, cleaning of institutions such as schools, hospitals etc, and cleaning of commercial premises such as factories, offices hotels etc. In particular, the compositions are effective for use on surfaces which may harbour soils having the potential for bacteriological contamination in surface imperfections, joints and other relatively confined regions.

For domestic use at least, the composition is preferably formulated as a product intended for application by spraying and is conveniently packaged in a suitable container, eg having a hand operated trigger spray or an aerosol propellant dispenser. The container is preferably light-opaque.

In use, the composition is applied to a surface to be cleaned in any convenient manner, eg by spraying from a suitable dispenser, wiping on with a carrier such as a cloth or sponge, or pouring from a container etc. In the case of toilet cleaning to disclose soil in toilet bowls the composition may be applied from rim blocks or from in-cistern devices as well as by spraying. Application might in some cases, particularly in industrial cleaning, be followed by exposure to a light source, eg a white light source such as a quartz halogen lamp or fluorescent "daylight" source. This would generally be followed by a rinsing step if required, eg by wiping with a carrier, application of a stream of running water etc. After use, any remaining coloured dye visible at the location of cleaning indicates remaining bound dye, generally indicative of the presence of remaining protein and thus indicating the need for further cleaning.

In embodiments using dyes fugitive to chemical treatment, such as Brilliant Blue G, which is fugitive on exposure to chlorine bleach as discussed above, the cleaning step may be followed by application of a suitable chemical reagent such as chlorine bleach to render substantially invisible any unbound dye or remaining dye absorbed into surfaces such as grouting or in scratches.

In a further aspect, the invention thus provides a method of cleaning a surface, comprising applying to the surface a composition in accordance with the invention, followed by rinsing.

The invention will be further described, by way of illustration, in the following Examples and by reference to the accompanying figures in which:

Figure 1 is a graph of colour difference versus % of non-ionic surfactant, showing results obtained with controls without solvent (indicated by crosses) and with three component mixtures including 15% of IPA (indicated by circles);

Figure 2 is a 3 dimensional perspective graph of the colour difference (DE) response surface for a range of compositions in accordance with the invention containing varying amounts of non-ionic surfactant (NI) and varying amounts of IPA;

Figure 3 is a 3 dimensional perspective graph of residue reduction (PDET) (indictive of cleaning efficacy) for a range of compositions in accordance with the invention containing varying amounts of non-ionic surfactant (NI) and varying amounts of IPA; and

Figure 4 is a graph of the ratio of light absorption to light scattering (K/S) versus wavelength (in nm) illustrating photofading of Rose Bengal and Erythrosin B on unglazed ceramic tile.

EXAMPLES

Dye Binding

Example 1

A solution of the protein bovine serum albumin (BSA) was applied to white glazed tiles in a band across each tile and the tiles dried (at 50°C) to provide a number of similarly soiled tiles which constitute model sources of soil.

Solutions were prepared of the acid dye Brilliant Blue G (BBG) and the acid dye Erythrosin B (EB) in water and in a range of surfactants typical of general purpose cleaning formulations at typical (user) concentrations of 0.5 and 2.5%. The following surfactants were used:

Non-ionic: C9-11 5EO (Imbentin 91-35)

Anionic: Primary Alkyl Sulphate (PAS) (Albright & Wilson, Empicol LX)
Secondary Alkane Sulphonate (Hoechst, Hostapur, Hostapur is a Trade Mark)
Linear AlkylBenzene Sulphonate (Petrelab 550, Petrelab is a Trade Mark)

Dye solution was sprayed onto the soiled tiles and the solution left in contact with the BSA bands. After 5 minutes, the tiles were rinsed by being held under cold running tap water for sufficient time to destain the background without washing bound dye from protein-dye complex, typically for about 5 seconds or less.

In each case, the amount of visibly perceptible colour was quantified by measuring the colour difference (as defined by the CIE (Commission Internationale de l'Eclairage) (1976) specifications for Illuminant D65) as compared with the original colour of the tile surface before staining as measured using an ICS MicroMatch Spectroreflectometer. The amount of colour difference is represented by a numerical value known as delta E. For further details of the technique used see RWG Hunt, Measuring Colour (2nd Ed.) Ellis Horwood, London, (1991). In general, a delta E value exceeding about 1 indicates a colour difference perceptible to the naked eye in these studies. In some cases, colour difference was assessed qualitatively by eye with a visible colour difference (indicative of a delta E value greater than about 1) indicated as "+", and no visible colour difference (indicative of a delta E value less than about 1) indicated as "-".

The results obtained are shown in Table 1.

The results of Table 1 show that with none of the formulations comprising surfactant plus dye was the dye able to bind to protein sufficiently for its disclosure, whereas control solutions comprising dye in water were able to do so.

Example 2

Factorial experiments were carried out, using the procedure generally as described in Example 1, using a range of three component formulations comprising propan-2-ol (IPA), the non-ionic surfactant Imbentin 91-35 and BBG or EB dye. A range of such three component formulations were prepared, with acetic acid being used to adjust pH to

between 3 and 4.

Tiles treated with BSA as described in Example 1 were sprayed with the formulations to reveal protein, briefly rinsed with cold tapwater and allowed to dry. The intensity of the resulting stains on the tiles was measured spectrophotometrically and delta E values representative of colour difference were calculated as described in Example 1. The results of these factorial experiments are shown in Tables 2 and 3.

Statistical analysis was carried out on the results obtained with BBG, as greater colour differences (delta E values) were obtained with this dye than with EB: this is in part due to the fact that EB binds less strongly to protein than BBG and is more easily rinsed out of the complex with water at the rinse stage, while the BBG/protein complex is stable to rinsing with water.

Statistical Analysis of Factorial Experiments with BBG

The data obtained were analysed using the general linear models procedure (PROC GLM) of the Statistical Analysis System (SAS). The SAS system is an integrated system of software developed by the SAS Institute Inc, SAS Campus Drive, Cary, NC 27513, USA. SAS is a registered Trade Mark. The GLM procedure uses the method of least squares to fit general linear models and is particlularly useful for the analysis of variance of experimental designs that may not be fully balanced (as in this study).

Consider first the results from experiments up to and including 0.1 percent nonionic surfactant (Table 3) which are balanced to some degree. Analysis of variance shows that the effect of changing dye concentration is highly significant (with greater than 99 percent confidence) in increasing the colour observed. In particular, there is surprisingly a triple interaction between the three variables dye, surfactant and solvent which is significant at the 94 percent confidence level. Put simply, an interaction means that the observed effect of one component depends on the level of another component. Within the stipulated experimental region, the signs of the parameters suggest that the main effect of both solvent and surfactant is to reduce the colour yield, but the interaction between solvent and surfactant, solvent and dye and surfactant and dye compensate. This means that the reduction in colour yield is less than expected when solvent and surfactant are present together. The model accounts for 91 percent of the variance and is significant at better than the 99 percent confidence level.

Analysis of all the data for a fixed level of dye (100 ppm) tends to confirm the presence of a positive solvent-surfactant interaction (significant at greater than 80 percent confidence).

Figure 1 is a graph comparing the results for controls run with 100 ppm Brilliant Blue G in Imbentin C91-35 solutions at around pH 3.5 but without solvent in the standardised test, with results for 3 component mixtures including IPA at a constant 15%. On this graph the threshold of perception (visibility threshold) is indicated by a horizontal line at the position of a colour diffence of 1. The graph shows that colour difference falls with increasing surfactant level, but it is increased by the presence of solvent.

The statistical analysis thus demonstrates the existence of a synergistic reaction between the solvent and surfactant, which is illustrated graphically in Figure 2.

Figure 2 is a 3 dimensional graph of variation of protein revelation, as represented by delta E (DE) values, in three component formulations comprising dye, solvent (IPA) and non-ionic surfactant (NI), and containing varying amounts of solvent and surfactant. If there were no interaction between solvent and surfactant in three component mixtures, the protein relvelation surface would be a flat surface, sloping downwardly with uniform slope for both increasing solvent concentration and increasing surfactant concentration, so that increasing either solvent or surfactant concentration would have a predictable, uniform, additive effect on the reduction in binding of dye to protein, indicated by a reduced value of delta E.

In fact, the protein revelation surface is not flat but is concave or saddle shaped showing that in three component mixtures of dye, solvent and surfactant the reduction in binding of dye to protein is less than the combined lowering effect of surfactant alone and solvent alone. A synergistic effect is thus occuring.

Example 3

The procedure of Example 2 was repeated, using ethanol as solvent in place of IPA, in formulations comprising 100 ppm Brilliant Blue G and varying amounts of Imbentin C91-35. The results are shown in Table 4.

Example 4

The procedure of Example 3 was repeated with formulations including as solvent Dowanol PnB obtained from Dow Chemical Company. (Dowanol is a Trade Mark.) Dowanol PnB comprises n-butoxy propan-2-ol (propylene glycol n-butyl ether). Dowanol PnB is miscible with water up to a level of about 6% depending on temperature and levels of isomers. The results are shown in Table 5.

Example 5

The procedure of Example 3 was repeated with formulations including ethylene glycol as solvent. Table 6 lists compositions which all gave perceptible staining in the standardised assessment procedure. In this case, the colour was more intense before rinsing.

Example 6

The procedure of Example 3 was repeated with formulations including the commercially available preparation known as Butyl Cellosolve (Cellosolve is a Trade Mark). Butyl Cellosolve comprises the water-miscible cleaning solvent 2-butoxy ethanol (also called ethylene glycol monobutyl ether). The results are shown in Table 7.

Example 7

The procedure of Example 2 was repeated, using formulations comprising non-ionic surfactant (Imbentin C91-35, 0.7 percent), propan-2-ol (15 percent) and Brilliant Blue G (100 ppm) and varying amounts of anionic surfactant (primary alkyl sulphate (PAS), Empicol LX) to investigate the tolerance to PAS, that is the amount of PAS that could be added before the soil-revealing effect is lost was determined.

PAS surfactant with Brilliant Blue G and added propan-2-ol was unable to reveal protein. Other results are summarised in Table 8. In the table a "(+)" signifies visually perceptible stain and "(-)" signifies that no stain could be seen in the standardised assessment.

Example 8

The procedure of Example 2 was repeated, using formulations containing the ether sulphate commercially available from Enichem under the Trade Mark Lialet 111 (average carbon chain length 11 with an average degree of ethoxylation of 3). These experiments clearly demonstrated the effect of added solvent "switching on" the protein revealing effect, as indicated in Table 9. As before, Brilliant Blue G was used at 100 ppm and solutions were adjusted to a pH of 3.5 with acetic acid.

Example 9

The procedure of Example 2 was repeated, using 1, 2-dimethoxyethane as solvent in place of IPA, in formulations comprising 100 ppm Brilliant Blue G and varying amounts of Imbentin C91-35. The results are shown in Table 10.

Cleaning

Example 10

Experiments were carried out to confirm that formulations which are effective at revealing protein are also effective at general purpose cleaning. Tests were conducted on a model kitchen soil on semi-matt ceramic tiles.

The model soil has the following composition:

	Weight Percent
Glycerol tripalmitate	1.0
Triolein	0.5
Kaolin	0.5
Liquid paraffin	0.2
Palmitic acid	0.1
Carbon black (Elftex 675)	0.02
Industrial Methylated Spirits	97.68

(Elftex is a trade name of Carbot Europa, Special Blacks Division, 25 Boulevard de l'Admiral Bruix, 75782 Paris Codex 16, France:)

The soil composition was mixed immediately before use for 30 minutes using a Silverson laboratory mixer/emulsifier, and was applied to tiles as follows.

i) Semi-matt ceramic tiles were cleaned with an abrasive cleaner, rinsed and dried at 50°C.

ii) The tiles were masked to leave exposed a central strip which was evenly sprayed with the soil composition using a Humbrol (Hull, England) Powerpack spraygun in a fumecupboard. The tiles were left to age for 24 hours before use.

iii) Microcellulose sponge cloths (from Tesco Supermarket) were cut to size, washed and rinsed several times in water to remove surface active residues, and dried. Dried cloths were dipped in water or the formulation under test and fitted to the cleaning head of a cleaning machine (see below). Excess solution was expressed from the cloth before use by placing the head on a plastic mesh over paper towel and loading the head with an appropriate weight for 30 seconds.

iv) Cleaning tests were carried out using a specially designed and constructed linear scrubbing machine operated under standard conditions and with a surface pressure of about 3 g/sq.cm to simulate hand pressure. After cleaning, the difference in colour of the cleaned strip from the clean tile was measured using a Dr Lange "Microcolor" colorimeter.

In experiments, soil was cleaned from a tile using just water and a measurement made of the colour difference of the residue remaining as compared with that of the clean tile. The percentage reduction of this residue by subsequent use of a formulation under test was then used as a measure of the effectiveness of the formulation over and above that of water alone.

The results for a number of formulations, all containing 100 ppm BBG dye and varying amounts of IPA and Imbentin 91-35 are shown in Table 11.

The results show that the combination of non-ionic surfactant and IPA is more effective at removing the simulated kitchen soil from the ceramic surface than water alone. Statistical analysis of the data set (with the assumption of a zero intercept) suggests (reasonably) that the main effect of both surfactant and solvent is positive in being better than water alone in reducing the residue. However, a negative interaction is also suggested. The effect of the interaction is illustrated in the accompanying graph of Figure 3 of the predicted response surface, showing the percent reduction in delta E relative to water for formulations including varying amounts of non-ionic surfactant (NI) and IPA. What the interaction amounts to is that the effect of either solvent or surfactant is reduced at the highest level of the other component compared to its effect at the lowest level.

All effects were significant at better than 98 percent confidence.

Fugitive Properties of Dyes

A series of further experiments were carried out to demonstrate the fugitive properties of various dyes. For simplicity these were generally performed using solutions of dye in water, rather than dye, solvent, surfactant mixtures, but it is expected that the fugitive properties of the dyes will not be affected by the presence of other components.

Example 11

Unglazed ceramic tiles (H & R Johnson Tiles Ltd) were used as a model for porous material such as grouting. Brilliant Blue G dye solution (2 ml, 100 ppm) was applied to tiles via a syringe. The solution spread out radially under capillary action to create a uniformly stained area suitable for instrumental measurement after drying for a short time in an oven (100°C). Replicate reflectance spectra of the stained and unstained tile were measured as in Example 1 (with the stained tile showing maximum absorbance at 620 nm).

In order to test the reaction of Brilliant Blue G to oxidation by chlorine bleach, the stained area was cleaned by wiping with a cellulose sponge cloth which had been moistened with cold tapwater, squeezed out and treated with Domestos Multi-Surface Cleaner (1ml). Immediately after cleaning, the cleaned area was rinsed thoroughly in cold running tapwater, dried as above and the reflectance spectrum remeasured. The loss of dye was determined from the change in the ratio of light absorption to light scattering (K/S) at the absorbance peak using Kubelka-Munk analysis (see D B Judd and G Wyszecki, Color in Business, Science and Industry, Wiley series in Pure and Applied Optics (3rd Ed.), London, John Wiley and Son (1975)) and found to be 99.7 per cent. The measured colour difference from the unstained tile was 0.5, on the threshold of perceptibility in a side-by-side comparison and below perceptibility in monadic presentation.

In a control experiment, washing up liquid was substituted for Domestos Multi-Surface Cleaner. In this case 81.2 per cent of the stain was removed, but a colour difference of 5.9 remained, easily seen in monadic presentation.

This example demonstrated that Brilliant Blue G dye is rapidly and effectively decolourised by dilute sodium hy-

pochlorite (the bleach in Domestos Multi-Surface Cleaner), even on porous tile.

Further experiments (details of which are not included) have demonstrated that the presence of protein makes no significant difference to the colour fugitive properties of Brilliant Blue G.

Example 12

In order to test the light fading properties of Brilliant Blue R dye, a similar procedure to that of Example 11 was followed, but using semi-matt white tiles treated with BSA.

However, in this case, the dye was allowed to dry on the tiles after briefly being rinsed with cold tapwater. The intensity of the stain on the tiles was measured spectrophotometrically as described above before exposure to an artifical daylight source (Atlas Weather-O-Meter) for 5 hours. After exposure, the intensity of the stain was removed and the amount of stain loss calculated using Kubelka-Munk analysis.

With Brilliant Blue R, about 50% colour loss was obtained after 5 hours exposure.

Example 13

The light fading properties of Acid Red 94 (Rose Bengal) were compared with those of Acid Red 51 (Erythrosin B) on porous tiles using the staining procedure given in Example 11. Care was taken to ensure that the initial reflectances of the stained tiles were of a similar magnitude so that the rate of fading results would not be unfairly weighted in favour of Rose Bengal. Both stains were simultaneously exposed to bright daylight through window glass on a window sill. After 4 hours, the reflectance spectra of the faded stains were remeasured.

The results are shown graphically in Figure 4. Unbroken lines show results before exposure: those for Rose Bengal are marked with a diamond; those for Erythrosin B are marked with a cross. Broken lines show results after exposure: those for Rose Bengal are marked with a solid square; those for Erythrosin B are marked with a star.

The total loss of chromophore in the visible region (400 - 700 nm) was measured as the percentage change in the sum of the Kubelka-Munk ratio of K/S (corrected for that of the clean tile). The Rose Bengal stain showed an average loss of 51 percent whereas the Erythrosin B stain showed an average loss of 41 percent.

Example 14

In a further comparison, the light fading properties of Rose Bengal and Erythrosin B were examined using a similar procedure to Example 13 except that light exposure was to artificial daylight (Atlas Weather-O-Meter) for 90 minutes. Under these conditions, 95 percent of the Rose Bengal and 90 percent of Erythrosin B faded. In terms of the colour difference from the original unstained tile (for which the smaller the difference the better the result) Rose Bengal had faded to 2.3 units compared to 3.4 units for Erythrosin B.

Example 15

In a further example, the light fading properties of Rose Bengal were examined on a porous tile previously sprayed with a dilute protein solution (1 percent bovine serum albumin) and dried (50°C). A similar procedure to that of Example 13 was followed by light exposure was to artificial daylight (Atlas Weather-O-Meter) for 90 minutes. Under these conditions, 86 percent of Rose Bengal and 85 percent of Erythrosin B faded. In terms of colour difference, in the presence of protein, Rose Bengal faded to 4.1 units compared to 4.9 units for Erythrosin B.

Example 16

In a further example, the light fading properties of Rose Bengal and Brilliant Blue G were examined on a porous tile.

A solution of Rose Bengal in distilled water (10ppm) was sprayed on a masked tile to give an even circular spot. The procedure was repeated with a solution of Brilliant Blue G in distilled water (10 ppm) to give an even circular spot on another location on the same tile. The reflectance spectrum of each spot was measured using an ICS MicroMatch spectroreflectometer after drying at 45 degrees Centigrade for about 1 hour. The tile was then exposed to daylight for 2 hours and the reflectance spectra remeasured. The percentage change in the summation of the Kubelka-Munk ratio of K/S in the range of 400 to 700 nm (corrected for that of the clean tile) was calculated for for the individual dyes. In this test the average total loss of chromophore for the Rose Bengal was 19 percent compared to the average total loss of chromophore for Brilliant Blue G of 45 percent.

Example 17

Tests were carried out on APS at a concentration of 100 ppm. in solution with non-ionic surfactant (Imbentin C91-35) at 0.7% and propan-2-ol at 10%, pH adjusted to 3.5. The procedure of Example 13 was generally followed except that light exposure was to artificial daylight (Atlas Weather-O-Meter) for 150 minutes. Under these conditions about 45% of the APS faded. It is believed ZPS will fade faster than this. APS has also been shown to be phototoxic to bacteria.

Phototoxic Properties of Dyes

A series of further experiments were carried out toshow the phototoxic effect of Rose Bengal in compositions with solvent and surfactant in suspension tests using the following bacteria:

Staphylococcus aureus	NCTC 6538	(Gram positive)
Escherichia coli	NCTC 8196	(Gram negative).

Organisms were grown up by overnight incubation in nutrient broth at 37°C. Cultures were isolated by vacuum filtration using a 0.45um Millipore filter and washed with quarter-strength Ringers solution before resuspension in Ringers solution (10 ml). The organisms in suspension were enumerated by serial dilution and plating with nutrient agar and the total viable count (TVC) expressed as the decadic logarithm of the number of colony-forming units (cfu) per ml.

Test solutions were made up in sterile plastic petri dishes to a depth of 5mm (30mls). A suspension of micro-organism (0.3ml) was added to each solution and gently mixed in. If Rose Bengal was to be included in the test solution it was added last to minimise light exposure.

Rose Bengal when used was present at a concentration of 20 ppm, although in some cases control solutions without Rose Bengal were exposed to light and the results for these are given in the following Examples in the columns headed "No Rose Bengal". Solutions were exposed for 20 minutes on a light box. The average intensity at the surface of the diffuser was 4000 lux measured with a Megatron DA 10 light meter (from Megatron Ltd). After exposure, surviving bacteria were enumerated as colony-forming units (cfu/ml) following incubation after serial dilution and plating onto agar. The decadic logarithm of the number of bacteria remaining (as colony-forming units per ml) was determined and compared to the number before exposure as log (start count) - log (final count). The higher the value, the greater the bacterial kill. Using this notation a value of zero means no change in the number of organisms following exposure to the conditions. The notation "+" preceding a log ratio figure indicates that no micro-organism growth could be observed (ie total kill).

A variety of tests were carried out all at pH 4, using reagents as specified in the following examples, and the results are given in the associated tables.

Example 18

Suspension tests were carried out using Rose Bengal, ethanol and Imbentin C91-35, with S. aureus. The decadic logarithm of the starting concentration, log (start), of S. aureus was 6.8. Results are given in Table 12.

Example 19

Suspension tests were carried out using Rose Bengal, Dowanol PnB and Imbentin C91-35, with S. aureus. Log (start) = 6.9. Results are given in Table 13.

This example shows that Dowanol PnB has certain biocidal properties.

Example 20

Suspension tests were carried out using Rose Bengal, ethylene glycol and Imbentin C91-35, with S. aureus. Log (start) = 6.8. Results are given in Table 14.

Example 21

Suspension tests were carried out using Rose Bengal, IPA and Lialet 111, with S. aureus. Lialet 111 is the trade name of an ether sulphate formulation commercially available from Enichem, having an average chain length 11 with an average degree of ethoxylation of 3. Log (start) = 6.7. Results are given in Table 15.

Example 22

Suspension tests were carried out using Rose Bengal, propan-2ol- and Imbentin C91-35, with E. coli. Log (start) = 6.8. Results are given in Table 16.

Example 23

Suspension tests were carried out using Rose Bengal, ethanol and Imbentin C91-35, with E. coli. Log (start) = 7.1. Results are given in Table 17.

TABLE 1

Detergent			Dye	
Type	Amount%	Type	Amount (ppm)	Delta E
--	---	BBG	20	3.48
--	---	BBG	100	13.67
--	---	EB	20	3.9
--	---	EB	100	3.9
Imbentin 91-35	0.5	BBG	20	-
Imbentin 91-35	0.5	EB	20	-
Imbentin 91-35	2.5	BBG	20	-
Imbentin 91-35	2.5	EB	20	-
Empicol LX	0.5	BBG	20	-
Empicol LX	0.5	EB	20	-
Empicol LX	2.5	BBG	20	-
Empicol LX	2.5	EB	20	-
Hostapur	0.5	BBG	20	-
Hostapur	0.5	EB	20	-
Hostapur	2.5	BBG	20	-
Hostapur	2.5	EB	20	-
Petrelab 550	0.5	BBG	20	-
Petrelab 550	0.5	EB	20	-
Petrelab 550	2.5	BBG	20	-
Petrelab 550	2.5	EB	20	-

TABLE 2

ERYTHROSIN B FACTORIAL EXPERIMENTS			
IPA (%)	DET (%)	EB (ppm)	DELTA E
5.0	0.05	20.0	2.94
10	0.05	20.0	1.21
5.0	0.1	20.0	2.38
10	0.1	20.0	0.68
5.0	0.05	100.0	3.65
10	0.05	100.0	2.44
5.0	0.1	100.0	2.19
10	0.1	100.0	2.21

TABLE 3

BRILLIANT BLUE G FACTORIAL EXPERIMENTS

IPA (%)	DET (%)	BBG (ppm)	DELTA E
0.0	0.0	20.0	3.48
0.0	0.0	20.0	4.08
5.0	0.05	20.0	1.30
5.0	0.05	20.0	4.23
5.0	0.1	20.0	2.81
5.0	0.1	20.0	3.33
10.0	0.05	20.0	2.10
10.0	0.05	20.0	4.33
10.0	0.1	20.0	2.31
10.0	0.1	20.0	3.73
0.0	0.0	100.0	13.67
0.0	0.0	100.0	12.2
5.0	0.05	100.0	13.09
5.0	0.1	100.0	9.43
5.0	0.1	100.0	11.61
10.0	0.05	100.0	12.36
10.0	0.05	100.0	14.54
10.0	0.1	100.0	5.99
10.0	0.1	100.0	9.88
10.0	0.1	100.0	7.19
10.0	0.1	100.0	10.22
10.0	0.1	100.0	6.05
10.0	0.1	100.0	10.61
10.0	0.2	100.0	7.96

10.0	0.4	100.0	5.26
10.0	0.5	100.0	6.8
10.0	0.6	100.0	5.28
10.0	0.7	100.0	5.26
10.0	0.8	100.0	1.96
10.0	1.0	100.0	2.71
10.0	1.2	100.0	2.48
15.0	0.2	100.0	6.65
15.0	0.4	100.0	3.85
15.0	0.6	100.0	5.05
15.0	0.8	100.0	4.04
15.0	1.0	100.0	2.61
15.0	1.2	100.0	1.80

TABLE 4

VISUALISATION OF BOVINE SERUM ALBUMIN ON GLAZED WHITE CERAMIC TILE USING BRILLIANT BLUE G (100 ppm): NONIONIC SURFACTANT AND ETHANOL			
Ethanol(%)	Imbentin C91-35(%)	pH	Delta E
5	0.2	3.5	7.3
5	0.4	3.5	3.7
5	0.6	3.5	1.8
10	0.2	3.5	7.9
10	0.4	3.5	3.8
10	0.6	3.6	2.9
15	0.2	3.7	6.7
15	0.4	3.7	6.0
15	0.6	3.6	3.3

TABLE 5

VISUALISATION OF BOVINE SERUM ALBUMIN ON GLAZED WHITE CERAMIC TILE USING BRILLIANT BLUE G (100 ppm): NONIONIC SURFACTANT AND DOWANOL PNB			
Dowanol PnB(%)	Imbentin C91-35(%)	pH	Delta E
1	0.7	3.5	2.5
2	0.7	3.5	3.0
3	0.7	3.5	3.6
4	0.7	3.6	3.0
5	0.7	3.6	4.0
6	0.7	3.6	4.4

TABLE 6

VISUALISATION OF BOVINE SERUM ALBUMIN ON GLAZED WHITE CERAMIC TILE USING BRILLIANT BLUE G (100 ppm): NONIONIC SURFACTANT AND ETHYLENE GLYCOL			
Ethylene Glycol (%)	Imbentin C91-35(%)	pH	Delta E
5	0.7	3.4	1.9
10	0.7	3.5	1.1
15	0.7	3.5	1.4

TABLE 7

VISUALISATION OF BOVINE SERUM ALBUMIN ON GLAZED WHITE CERAMIC TILE USING BRILLIANT BLUE G (100 ppm): NONIONIC SURFACTANT AND 2-BUTOXY ETHANOL			
2-Butoxy Ethanol (%)	Imbentin C91-35(%)	pH	Delta E
5	0.7	3.5	3.5
10	0.7	3.6	3.6
15	0.7	3.5	3.5

TABLE 8

VISUALISATION OF BOVINE SERUM ALBUMIN: EFFECT OF EMPICOL LX ON PROTEIN DISCLOSURE IN A MIXED ACTIVE FORMULATION WITH BRILLIANT BLUE G (100 ppm)				
Imbentin C91-35 (%)	Empicol LX (%)	Propan-2-ol	pH	Delta E
0.7	0.056	15	3.8	1.9 (+)
0.7	0.112	15	3.9	1.1 (+)
0.7	0.168	15	3.3	1.4 (+)
0.7	0.224	15	3.3	1.3 (+)
0.7	0.28	15	3.4	0.9 (+)
0.7	0.42	15	3.4	(-)

TABLE 9

VISUALISATION OF BOVINE SERUM ALBUMIN: PROTEIN DISCLOSURE WITH ETHER SULPHATE AND SOLVENT (BRILLIANT BLUE G 100 ppm, pH 3.5)			
	Surfactant (%)		
	0.1	0.5	1.0
Propan-2-ol (%)			
0	(v.faint)	-	-
5	+	-	-
10	+	(uneven)	(v. uneven)
15	+	+	+

TABLE 10

VISUALISATION OF BOVINE SERUM ALBUMIN ON GLAZED CERAMIC TILE USING BRILLIANT BLUE G (100 ppm): NONIONIC SURFACTANT AND 1, 2-DIMETHOXYETHANE			
1, 2-Dimethoxyethane (%)	Imbentin C91-35	pH	Delta E
5	0.7	4	2.6
10	0.7	4	1.8

TABLE 10 (continued)

VISUALISATION OF BOVINE SERUM ALBUMIN ON GLAZED CERAMIC TILE USING BRILLIANT BLUE G (100 ppm): NONIONIC SURFACTANT AND 1, 2-DIMETHOXYETHANE			
1, 2-Dimethoxyethane (%)	Imbentin C91-35	pH	Delta E
15	0.7	4	2.3

TABLE 11

EFFECTIVENESS OF FORMULATION IN REMOVAL OF RESIDUE LEFT AFTER CLEANING MODEL SOIL WITH WATER ONLY		
IPA(%)	DET(%)	PERCENT REDUCTION (DELTA E)
5.0	0.2	78.07
5.0	0.7	85.79
5.0	1.2	87.37
10.0	0.2	71.55
10.0	0.7	71.05
10.0	1.2	86.89
15.0	0.2	77.48
15.0	0.7	81.9
15.0	1.2	86.48

TABLE 12

		Log (ratio)	
Ethanol %	Imbentin C91-35 %	After Light Exposure	No Rose Bengal
5	0.2	+6.8	
5	0.6	4.6	
10	0.6	+6.8	
15	0.6	+6.8	
5	-	+6.8	0.1
10	-	+6.8	-0.4
15	-	+6.8	0.0
-	0.2	4.6	2.5
-	0.6	3.5	2.3
-	-	+6.8	2.3

TABLE 13

		Log (ratio)	
Dowanol %	Imbentin C91-35 %	After Light Exposure	No Rose Bengal
3	0.7	+6.9	
3	-	+6.9	4.0
-	0.7	5.2	3.4
-	-	+6.9	

TABLE 14

		Log (ratio)	
Ethylene Glycol %	Imbentin C91-35 %	After Light Exposure	No Rose Bengal
10	0.7	+6.8	
10	-	+6.9	-0.2
-	0.7	+6.8	3.4
-	-	+6.8	

TABLE 15

		Log (ratio)	
Propan-2-ol %	Lialet 111 %	After Light Exposure	No Rose Bengal
15	0.5	+6.7	
15	-	+6.7	4.9
-	0.5	+6.7	+6.7
-	-	+6.7	

TABLE 16

		Log (ratio)	
Propan-2-ol %	Imbentin C91-35 %	After Light Exposure	No Rose Bengal
5	0.1	2.3	
10	0.1	+6.8	
10	0.5	+6.8	
10	0.7	+6.8	
-	-	4.8	
5	-	5.5	0.3
10	-	3.0	1.9
-	0.1	1.2	1.3
-	0.5	1.0	1.2
-	0.7	1.1	1.1

TABLE 17

		Log (ratio)	
Ethanol %	Imbentin C91-35 %	After Light Exposure	No Rose Bengal
5	0.2	4.1	
15	0.6	+7.1	
5	-	5.0	0.2
10	-	+7.1	0.2
15	-	+7.1	2.2
-	0.2	3.3	2.5
-	0.6	3.4	2.6
-	-	3.9	

Claims

1. An acidic aqueous hard surface cleaning composition comprising dye which is substantive to protein; water-miscible solvent; and surfactant, the composition being effective to clean a surface and also to indicate the presence

of soil remaining on the surface by binding of dye to protein.

2. A composition according to claim 1, wherein the dye is an acid dye.

3. A composition according to claim 2, wherein the dye is selected from the group comprising Brilliant Blue G (Acid Blue 90, C.I. 42655), Brilliant Blue R (Acid Blue 83, C.I. 42660), C.I. Acid Blue 104, C.I. Acid Blue 109, Acid Violet 17 (C.I. 42650), Erythrosin B (Acid Red 51, C.I. 45430), Rose Bengal (Acid Red 94, C.I. 45440), aluminium phthalocyanine sulphonate, zinc phthalocyanine sulphonate and mixtures thereof.

4. A composition according to claim 1, 2 or 3, wherein the dye is such that the colour thereof disappears under suitable conditions.

5. A composition according to claim 4, wherein the dye is photosensitive.

6. A composition according to any one of the preceding claims, wherein the dye is capable of photo-dynamic inactivation of micro-organisms.

7. A composition according to claim 6, wherein the dye generates singlet oxygen on exposure to light.

8. A composition according to any one of the preceding claims, having a pH in the range 3 to 5.

9. A composition according to any one of the preceding claims, wherein dye is present in an amount in the range 10 to 100 ppm.

10. A composition according to any one of the preceding claims, wherein the solvent is polar.

11. A composition according to claim 10, wherein the solvent is a straight or branched chain C2 to C5 alcohol.

12. A composition according to any one of the preceding claims, wherein solvent is present in an amount in the range 2 to 20% by weight of the total weight of the composition.

13. A composition according to any one of the preceding claims, wherein the surfactant is alkoxylated.

14. A composition according to claim 13, wherein the surfactant is ethoxylated.

15. A composition according to any one of the preceding claims, wherein the surfactant is predominantly non-ionic.

16. A composition according to claim 15, wherein the surfactant comprises a mixture of non-ionic and anionic surfactant and the weight ratio of non-ionic to anionic surfactant is at least 3:1.

17. A composition according to any one of the preceding claims, wherein surfactant is present in an amount in the range 0.05 to 2.5% by weight of the total weight of the composition.

18. A composition according to any one of the preceding claims, further comprising detergent booster.

19. A method of cleaning a surface, comprising applying to the surface a composition in accordance with any one of the preceding claims, followed by rinsing.

Patentansprüche

1. Ein saures wässeriges Reinigungsmittel für harte Oberflächen, enthaltend Farbstoff, der unabhängig von Protein ist; wassermischbares Lösungsmittel; und Surfactant, wobei die Zusammensetzung wirksam ist, um eine Oberfläche zu reinigen und auch die Anwesenheit von Schmutz anzuzeigen, der auf der Oberfläche zurückbleibt, durch Binden des Farbstoffs an Protein.

2. Eine Zusammensetzung nach Anspruch 1, worin der Farbstoff ein saurer Farbstoff ist.

3. Eine Zusammensetzung nach Anspruch 2, worin der Farbstoff aus der Gruppe, umfassend Brilliant Blue G (Acid Blue 90, C.I. 42655), Brilliant Blue R (Acid Blue 83, C.I. 42660), C.I. Acid Blue 104, C.I. Acid Blue 109, Acid Violet 17 (C.I. 42650), Erythrosin B (Acid Red 51, C.I. 45430), Bengalrosa (Acid Red 94, C.I. 45440), Aluminiumphthalocyaninsulfonat, Zinkphthalocyaninsulfonat, und Mischungen derselben, ausgewählt ist.

4. Eine Zusammensetzung nach einem der Ansprüche 1, 2 oder 3, worin der Farbstoff ein solcher ist, daß die Farbe desselben unter geeigneten Bedingungen verschwindet.

5. Eine Zusammensetzung nach Anspruch 4, worin der Farbstoff lichtempfindlich ist.

6. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin der Farbstoff der photodynamischen Inaktivierung von Mikroorganismen fähig ist.

7. Eine Zusammensetzung nach Anspruch 6, worin der Farbstoff bei Belichtung Singulett-Sauerstoff erzeugt.

8. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, die einen pH-Wert im Bereich von 3 bis 5 aufweist.

9. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin der Farbstoff in einer Menge im Bereich von 10 bis 100 ppm vorhanden ist.

10. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Lösungsmittel polar ist.

11. Eine Zusammensetzung nach Anspruch 10, worin das Lösungsmittel ein gerad- oder verzweigtkettiger C_{2-5}-Alkohol ist.

12. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Lösungsmittel in einer Menge im Bereich von 2 bis 20 Gewichtsprozent des Gesamtgewichts der Zusammensetzung vorhanden ist.

13. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Surfactant alkoxyliert ist.

14. Eine Zusammensetzung nach Anspruch 13, worin das Surfactant ethoxyliert ist.

15. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Surfactant überwiegend nichtionisch ist.

16. Eine Zusammensetzung nach Anspruch 15, worin das Surfactant eine Mischung von nichtionischem und anionischem Surfactant umfaßt und das Gewichtsverhältnis von nichtionischem zu anionischem Surfactant zumindest 3 : 1 ist.

17. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Surfactant in einer Menge im Bereich von 0,05 bis 2,5 Gewichtsprozent des Gesamtgewichts der Zusammensetzung vorhanden ist.

18. Eine Zusammensetzung nach einem der vorstehenden Ansprüche, die ferner einen Detergens-Verstärker enthält.

19. Ein Verfahren zur Reinigung einer Oberfläche, umfassend das Aufbringen einer Zusammensetzung nach einem der vorstehenden Ansprüche auf die Oberfläche, und anschließendes Spülen.

Revendications

1. Composition de nettoyage pour surfaces dures acide aqueuse comprenant un colorant qui est substantif aux protéines, un solvant miscible dans l'eau, et un tensioactif, la composition étant efficace pour nettoyer une surface et également pour indiquer la présence de salissures restant à la surface par liaison du colorant aux protéines.

2. Composition selon la revendication 1, dans laquelle le colorant est un colorant acide.

3. Composition selon la revendication 2, dans laquelle on choisit le colorant parmi Brilliant Blue G (Acid Blue 90, CI

42655), Brilliant Blue R (Acid Blue 83, C.I 42660), C.I Acid Blue 104, C.I Acid Blue 109, Acid Violet 17 (C.I 42650), Erythrosin B (Acid Red 51, C.I 45430), Rose Bengal (Acid Red 94, C.I 45440), le phtalocyanine-sulfonate d'aluminium, le phtalocyanine-sulfonate de zinc et leurs mélanges.

4. Composition selon la revendication 1, 2, ou 3, dans laquelle le colorant est tel que sa couleur disparaît dans des conditions appropriées.

5. Composition selon la revendication 4, dans laquelle le colorant est photosensible.

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le colorant est capable d'inactivation photo-dynamique des micro-organismes.

7. Composition selon la revendication 6, dans laquelle le colorant produit un oxygène singulet lors de l'exposition à la lumière.

8. Composition selon l'une quelconque des revendications précédentes, qui a un pH dans la gamme de 3 à 5.

9. Composition selon l'une quelconque des revendications précédentes, dans laquelle le colorant est présent en une quantité dans la gamme de 10 à 100 ppm.

10. Composition selon l'une quelconque des revendications précédentes, dans lequel le solvant est polaire.

11. Composition selon la revendication 10, dans laquelle le solvant est un alcool en C_{2-5} à chaîne droite ou ramifiée.

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle le solvant est présent en une quantité dans la gamme de 2 à 20% en poids du poids total de la composition.

13. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif est alcoxylé.

14. Composition selon la revendication 13, dans laquelle le tensioactif est éthoxylé.

15. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif est principalement non ionique.

16. Composition selon la revendication 15, dans laquelle le tensioactif comprend un mélange de tensioactifs non ionique et anionique et le rapport pondéral du tensioactif non ionique au tensioactif anionique est d'au moins 3:1.

17. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif est présent en une quantité dans la gamme de 0,05 à 2,5% en poids du poids total de la composition.

18. Composition selon l'une quelconque des revendications précédentes, comprenant en outre un agent de renforcement de détergence.

19. Procédé de nettoyage d'une surface, consistant à appliquer à la surface une composition selon l'une quelconque des revendications précédentes, puis à rincer.

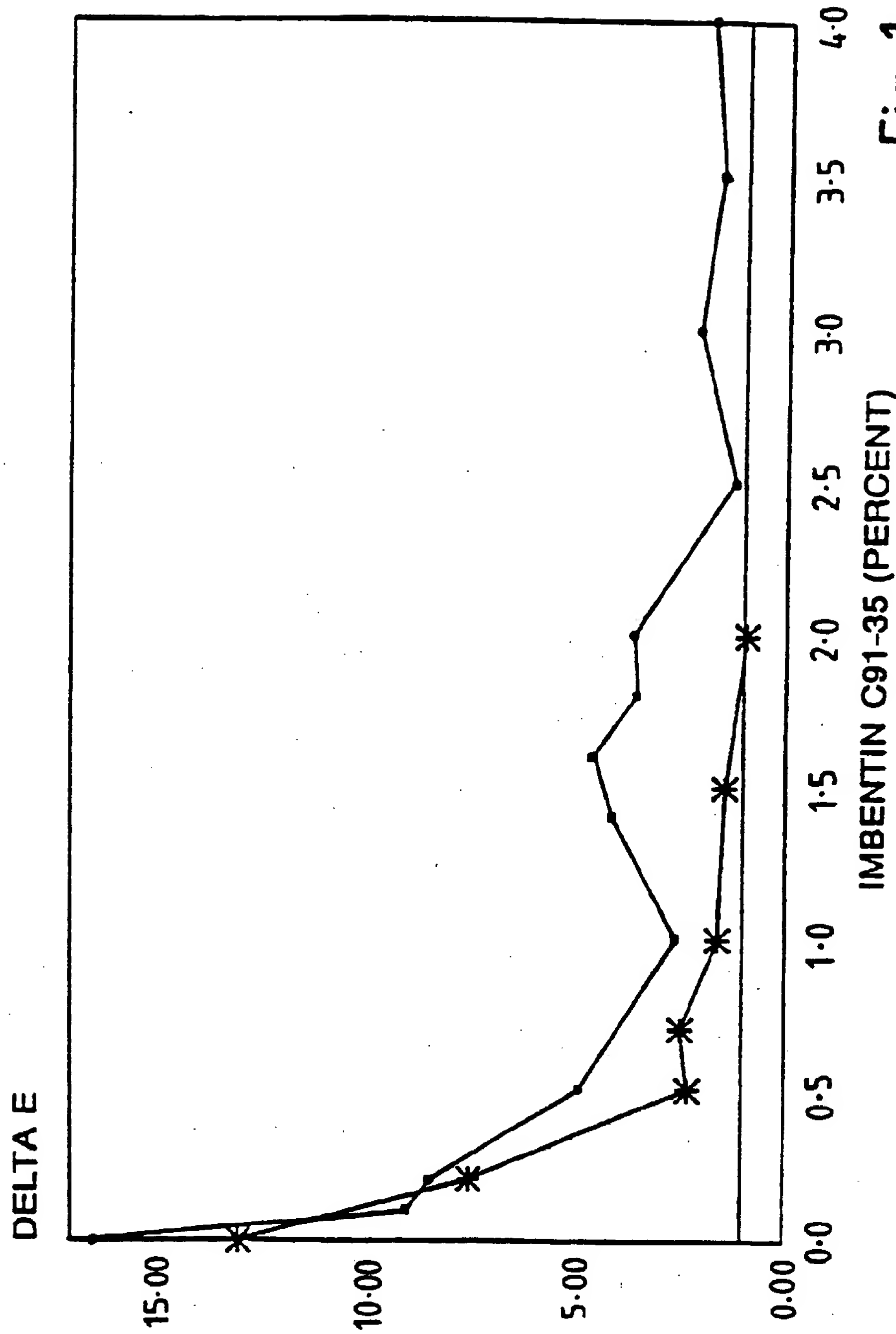
DELTA E
15·00
10·00
5·00
0·00
0·0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
IMBENTIN C91-35 (PERCENT)

Fig. 1

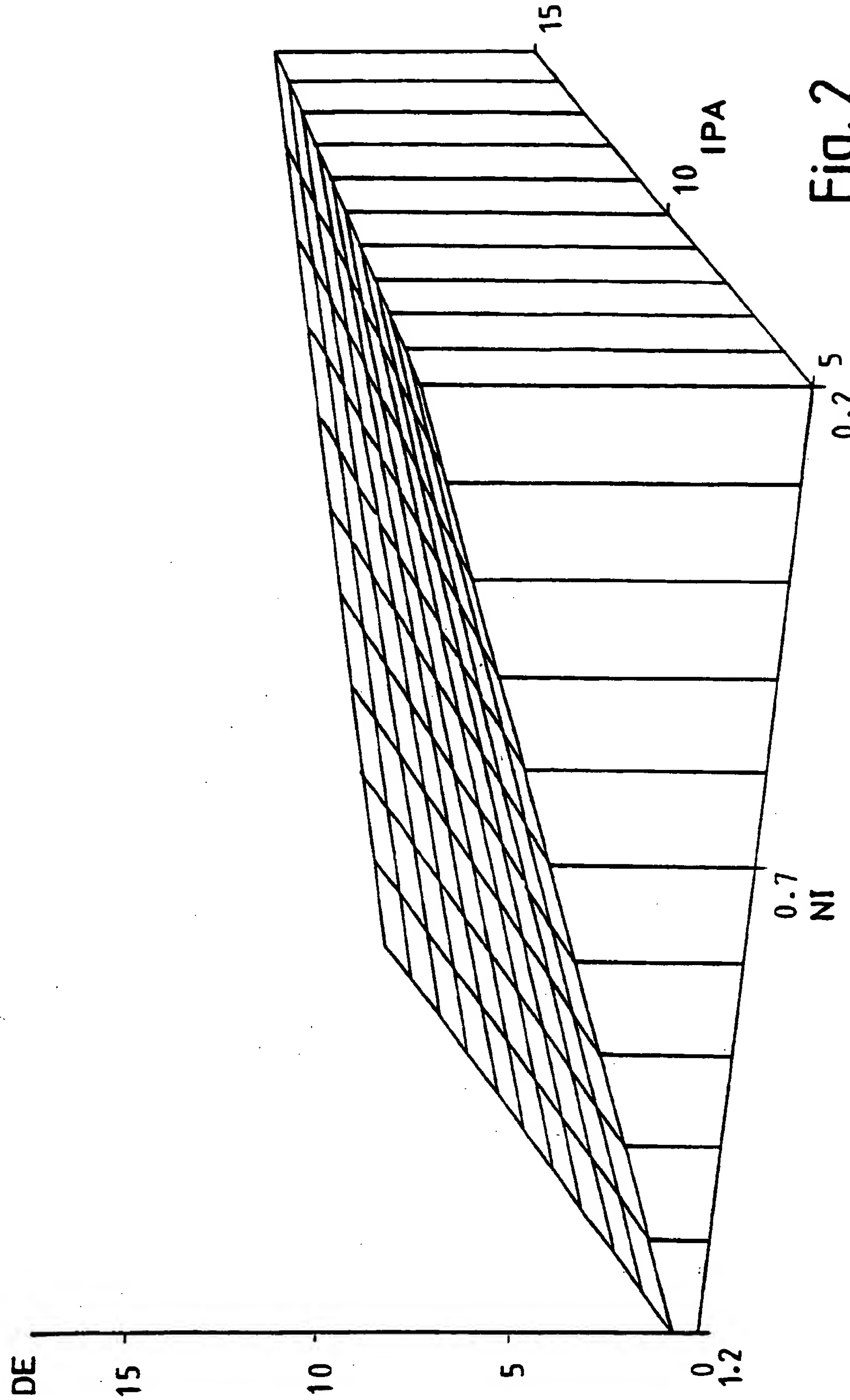

Fig. 2

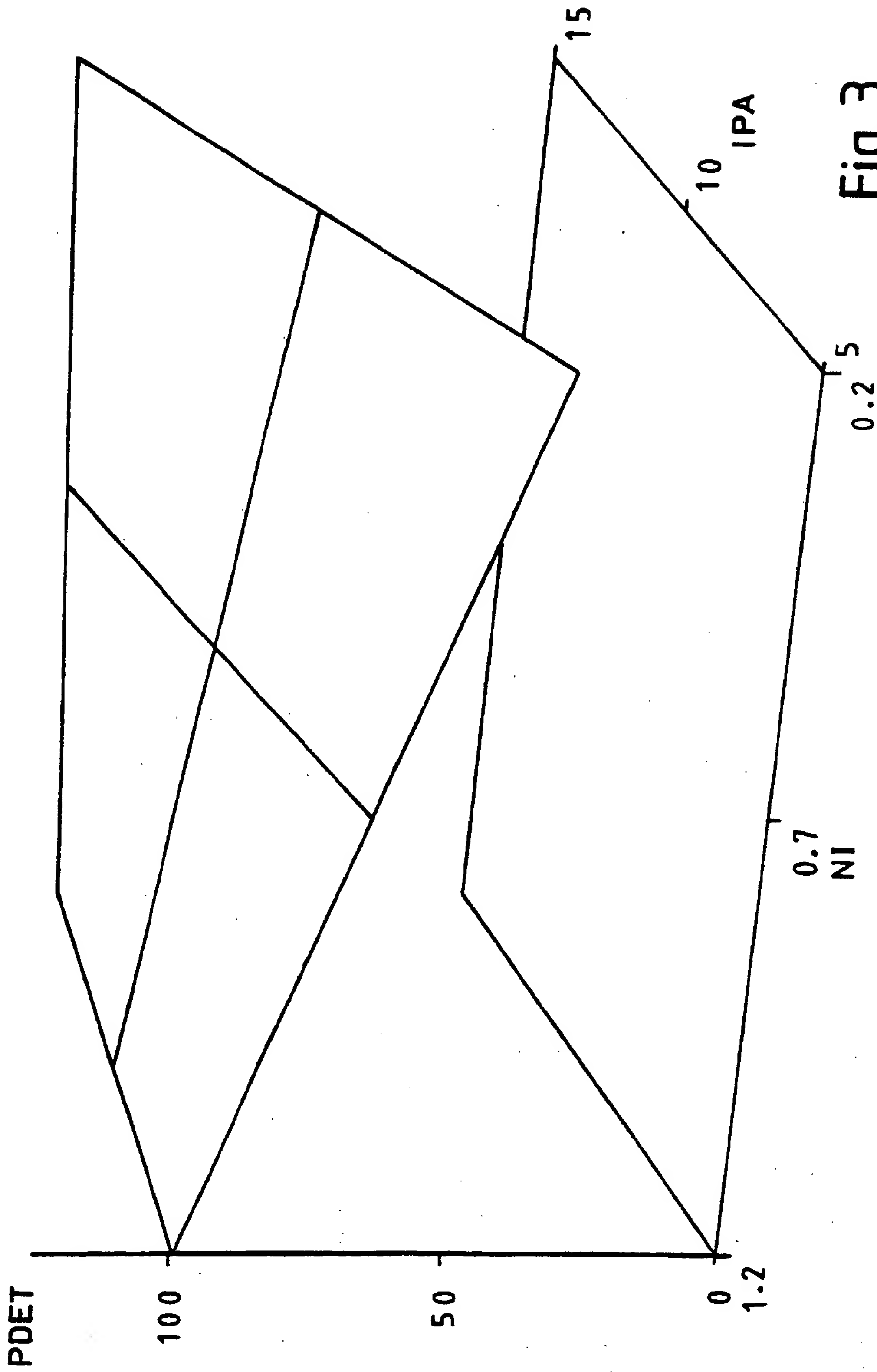

Fig. 3

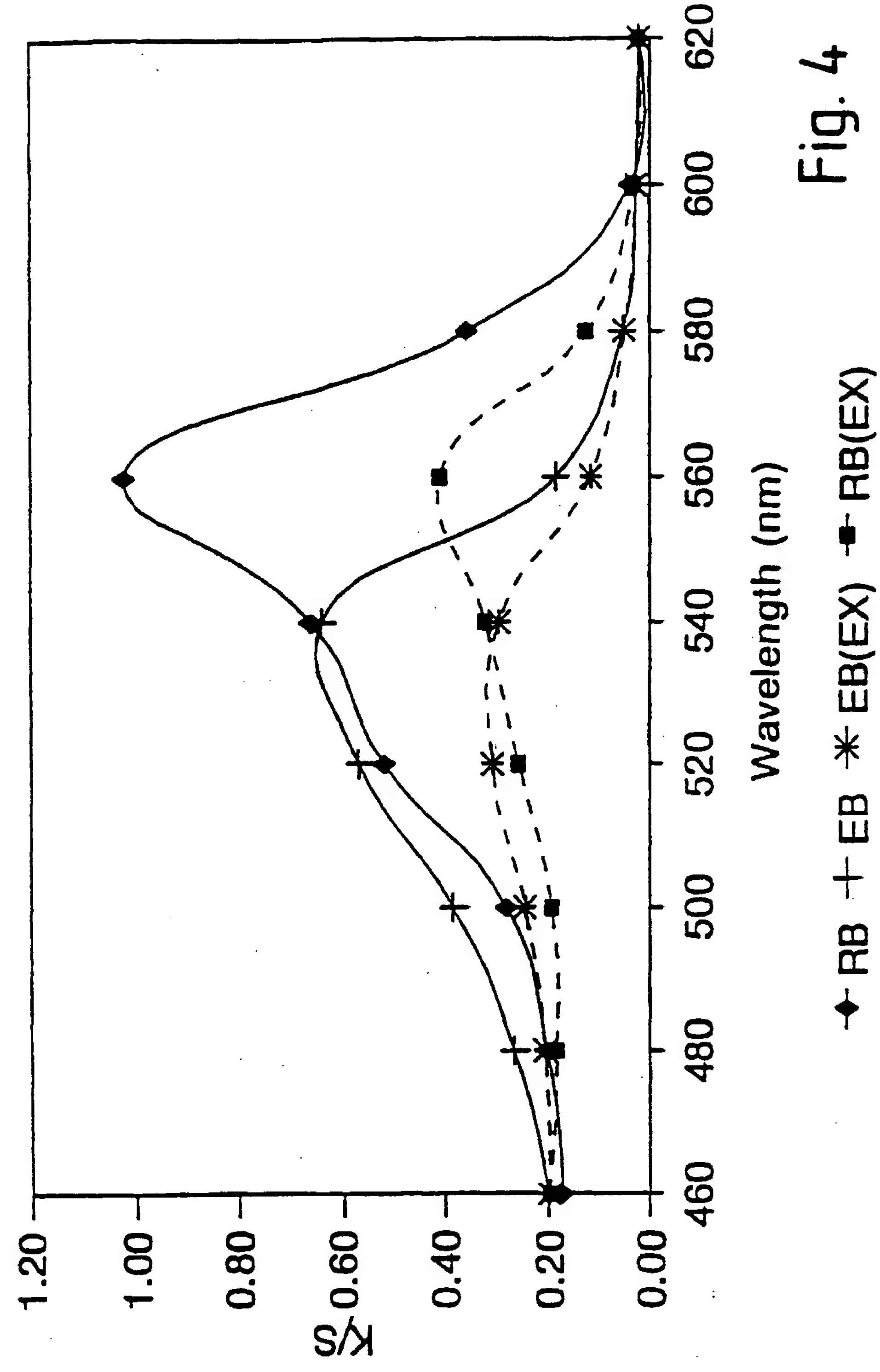
K/S
1.20
1.00
0.80
0.60
0.40
0.20
0.00
460
480
500
520
540
560
580
600
620
Wavelength (nm)
RB
EB
EB(EX)
RB(EX)

Fig. 4